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Studies Of Trimethylene Oxide.

STUDIES OF TRIMETHYLENE OXIDE

BY

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B. S. New Hampshire College, 1914

THESIS

Submitted in Partial Fulfillment of the Requirements for the

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May 31, 1916

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY DON WARREN BISSELL

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INTRODUCTION

These studies were undertaken preliminary to the synthesis of the cyano acids of the general formula $NC(CH_2)_nCO.OH$. An attempt was first made to synthesize the 6-cyano-hexanoic acid from n-hexanoic acid itself. N-hexanoic acid was successfully prepared in small quantities, but the process was tedious, There is little hope that the cyanide group can be introduced in the proper position, and give sufficient material for further investigation. Since, however,n-butyl-malonic ester is formed as an intermediate product in the synthesis of n-hexanoic acid,and had never been carefully studied, a short time was devoted to an investigation of the properties of this compound.

At present there is considerable hope that trimethylene oxide will give a general method of preparing the cyano acids mentioned above, since this compound is admirably suitable for extending the normal carbon chain three atoms at a time. Previous to this work, the preparation of trimethylene oxide had not been carried out in a feasible manner, and its properties had not been completely studied. In this thesis, a method of synthesis has been worked out, and the physical and chemical properties of the substance have been thoroughly investigated.

In this work, the synthetic value of trimethylene oxide has been demonstrated in one instance by the action of magnesium propyl bromide upon the oxide, which gave a sixty per cent yield of hexanol-1.

PART I.

N-BUTYL MALONIC ESTER.

THEORETICAL.

N-butyl-malonic ester was proven to be a pure substance by the determination of its boiling point under several pressures, the liquid distilling constant at each pressure. Its quantitative analysis showed it to have the theoretical quantity of carbon and hydrogen. Its atomic linking formula was established in its synthesis by the well known malonic ester methods, and by its decomposition into butyl malonic acid and finally into n-hexanoic acid, both of which are known.

By interpolation from the accompanying diagram (page 6), the boiling point of n-butly-malonic ester can be estimated at any pressure between 6.5 and 760 millimeters. The diagram shows that as the pressure approaches a perfect vacuum, a slight difference in pressure produces a very wide variation in the boiling point of the ester.

From the density diagram, it is apparent that the density of butyl-malonic ester is a linear function of the temperature, obeying the equation:

$$D = 0.9987 + 0.00095t$$

where D is the density of n-butyl-malonic ester, the density of water at 4^{0} being taken as unity. From this equation, the density of the substance can be computed at any temperature with a fair degree of accuracy.

N-BUTYL MALONIC ESTER

EXPERIMENTAL

PREPARATION OF N-BUTYL BROMIDE.

The n-butyl bromide was prepared by the action of hydrobromic acid upon the alcohol. Kahlbaum's n-butyl alcohol was redistilled to insure purity. The product used, boiled at 114-115° (uncor.). To 40 grams of this alcohol, was added 280 grams of constant boiling hydrobromic acid solution. The mixture was then boiled under the reflux . Action started as soon as the liquid was heated to boiling, and the n-butyl-bromide began to separate as an oil. After 45 minutes heating the oil was separated in a separatory funnel, and the aqueous layer again refluxed, this time for two hours. 60 grams of the crude oil was thus obtained, which on redistillation yielded 40 grams of pure butyl bromide boiling at 98.5-98.6 (uncor.), a yield of 50 percent

PREPARATION OF N-BUTYL MALONIC ESTER.

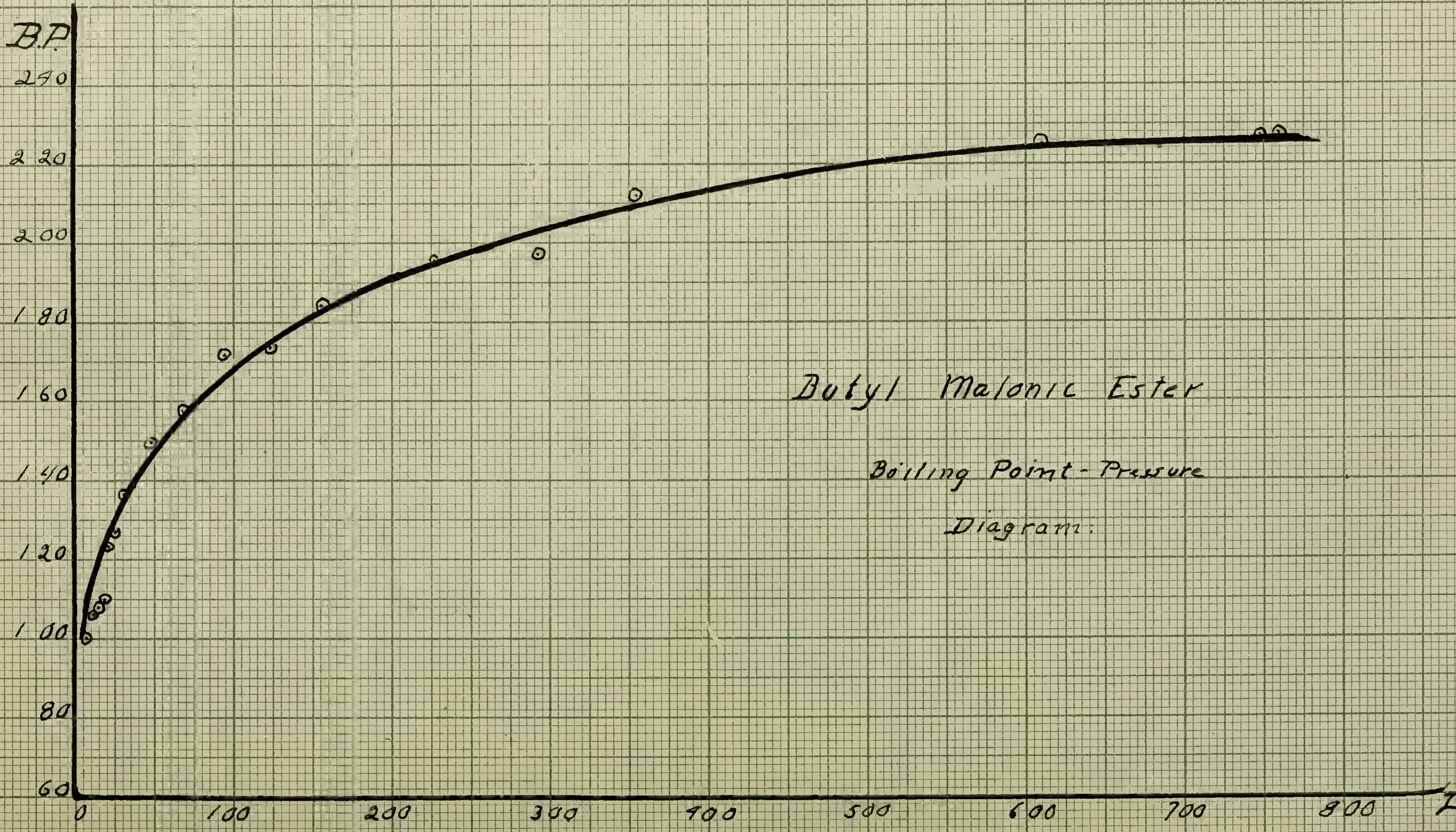
To 150 cc of absolute alcohol, was added slowly 7 grams of freshly cleaned sodium. The resulting sodium alcoholate solution was cooled in an ice bath. Then 49 gms of pure dry malonic ester was added drop by drop from a dropping funnel at the top of the condenser. This cooling was necessary to prevent saponification of the ester to the sodium salt of the acid. A white solid was formed at the bottom of the alcoholic solution. To the mixture was now added the 40 gms of n-butyl bromide, in small portions. There was no evidence of heat. The mixture was

then heated in a metal bath, and refluxed for eight hours. The alcohol was then distilled from the mixture and the residue dissolved in water. The n-butyl-malonic ester formed was extracted with ether and the ether extract dried over anhydrous sodium sulfate. The ether was evaporated and the residue distilled under diminished pressure. The pressure varied from 28-43 mm and the boiling point, from 120-152°. 40 gms of a light yellow oil was obtained, and this was redistilled under diminished pressure. Distillation began at a temperature of 130° with a pressure of 30 mm. Here the pressure remained fairly constant, and the liquid distilled over at a temperature varying from 136 to 139°. Analyses of the product for carbon and hydrogen gave the following results, the elements being weighed as carbon dioxide and water respectively:

	Theory	FoundI	II
Carbon	61.1	60.5	60.8
Hydrogen	9.27	9.05	9.16

The boiling point of n-butyl-malonic ester was determined with standard thermometers over a wide range of pressures. The results obtained, with the boiling points corrected are shown in the following table. The accompanying diagram shows the effect graphically.

Pressure (mm)	Temperature	Pressure	Temperature
6.5	101	70	159
17.0	111	95	173
16.5	109	122	175.5
13	107	156	184
20	124.5	293	196
11	106	227	196
25	129	353	212
33	138	512	221
49	151	612	226
51	154	750	227



Butyl Malonic Ester

Boiling Point - Pressure

Diagram.

U. OF I. S. S. FORM 3

The boiling point of n-butyl malonic ester at ordinary pressures was determined by the equilibrium method, using a standard thermometer. Three readings gave, after the necessary corrections had been made, a boiling point of 227.5°.

The index of refraction of this compound was determined using the Abbe' refractometer with ordinary light. The following readings were made at 20°.

1.6990	1.6988	1.6989
1.6990	1.6989	1.6990

From these readings, the index is- 1.6989 ± 0.0001

The density of n-butyl-malonic ester was determined using a specific gravity bottle. The bottle was calibrated at three different temperatures with the following results:

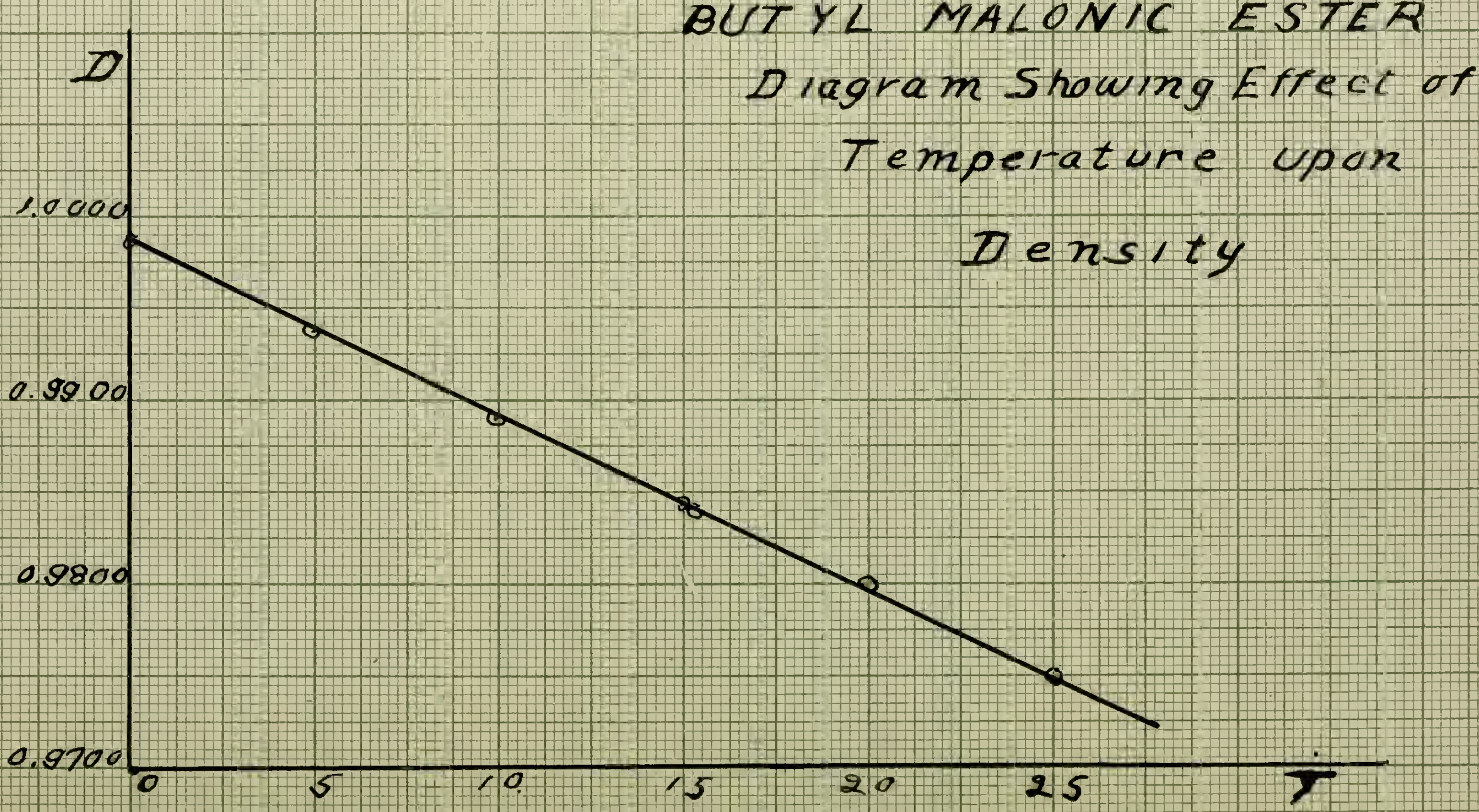
Temp.	Wt bottle and water	Wt of bottle	Wt of water	Density of water	Volume of bottle
28.5	11.2166	6.0100	5.2066	0.996115	5.2269
25.5	11.2216	6.0100	5.2116	0.996941	5.2276
25.0	11.2220	6.0100	5.2120	0.997071	5.2272

The volume of the bottle is taken as 5.227

With n-butyl malonic ester, the following results were obtained:

Temp.	Bottle and est.	Bottle	Ester	Density
0	11.2296	6.0100	5.2196	0.9986
5	11.2035	6.0100	5.1935	0.9936
10	11.1784	6.0100	5.1484	0.9888
15	11.1540	6.0100	5.1440	0.9841
15.5	11.1516	6.0100	5.1416	0.9836
20	11.1320	6.0100	5.1220	0.9800
20	11.1324	6.0100	5.1224	0.9800
20	11.1328	6.0100	5.1228	0.9800
25	11.1071	6.0100	5.0971	0.9750
25	11.1061	6.0100	5.0961	0.9750
25	11.1064	6.0100	5.0964	0.9750
25	11.1069	6.0100	5.0969	0.9750

These densities are relative to water at 4° C.



BUTYL MALONIC ESTER
Diagram Showing Effect of
Temperature upon
Density

U. OF I. S. S. FORM 3

N-BUTYL-MALONIC ACID.

To 4 gms of the n-butyl malonic ester was added 25 cc of a 25 percent solution of potassium hydroxide, and the mixture boiled under the reflux for two hours. It was then acidified with 30 percent sulphuric acid solution, and the n-butyl-malonic acid liberated extracted with ether. The ether was evaporated, and the acid crystallized from water. This acid melted at 101°. It has already been studied by Hell and Lumpp.[1]

N-HEXANOIC ACID.

About 2 gms of pure n-butyl-malonic acid was heated in a small test tube which was immersed in a sulfuric acid bath. When the bath had reached a temperature of 102°, the crystals melted, and at 135°, bubbles of carbon dioxide began to be evolved. At the end of two and a half hours, the decomposition was complete. The resulting oil was distilled from the metal bath, boiling constant at 202.5° (uncor.). It was a colorless liquid having the characteristic odor of hexanoic acid.

PART II

TRIMETHYLENE OXIDE

HISTORICAL.

Ethylene Oxide.

Ethylene oxide was first prepared by A. Wurtz[2], who noticed the evolution of a vapor, when a solution of potassium hydroxide was added to ethylene chlorhydrin. The vapor was dried by passing it over calcium chlorid, and condensed in a reciever immersed in a freezing mixture. The product was analyzed, and found to contain the theoretical amount of carbon and hydrogen to conform to the formula C_2H_4O, being isomeric with acetaldehyde with which it was probably mixed. By treating the product with phosphorous pentachlorid, however, Wurtz obtained an oil, whose physical properties were identical with those of the "Oil of the Dutch Chemists" - ethylene chlorid.

In a subsequent paper[3], Wurtz describes extensively the properties of ethylene oxide. He found that ethylene oxide is not obtained by the oxidation of ethylene, nor by dehydrating the glycol. Ethylene oxide is a very active compound and is capable of direct union with a large number of substances. It will unite with hydrogen to form ethyl alcohol, and with water to form glycol. By oxygen it is oxidised to glycollic acid. It reacts with bromine to form red crystals having the molecular formula $2(C_2H_2O)Br_2$. With acids, esters of glycol are formed, and with ammonia it unites to form oxygen bases. Wurtz compared the ethylene radical in its chemical behavior, to divalent metallic elements, and decided the analogy was very close. He

decided that the ethylene radical was basic, forming compounds analogous to metallic oxides, chlorides and hydroxides. Having kept a sample of ethylene oxide a year Wurtz[4] discovered by accident that it had become solid, and analysis showed that a polymer had been formed. Subsequent investigation showed that the polymerization could be hastened by adding a piece of fused potassium hydroxide or zinc chlorid to the liquid. Neither calcium chlorid or hydrochloric acid had any effect.

A modification of Wurtz's method of preparing ethylene oxide was discovered by Demole[5]. Instead of using the chlorhydrin of glycol, Demole used the chlor acetate, chloro-ethyl acetate. In this way, the saponification of the ester and the subsequent action to the oxide were carried out together. In drying the product by passing it over solid potassium hydroxide, Demole found that the potassium hydroxide became heated, and concluded that there was a chemical reaction between the product and the alkali. So Demole dried his product by distillation which he found gave equally good results. He found that the acetate method of preparing ethylene oxide increased the yield nearly two-fold.

Several years after the work of Demole, other methods of preparing ethylene oxide were investigated by Greene[6], who studied the action of metallic oxides on the ethylene halides. He found that ethylene oxide was formed when silver oxide was heated with ethylene bromide or ethylene iodide, the former

reaction requiring a temperature of 250°, the latter only 150°. With sodium oxide and ethylene bromide, the reaction took place at 180°. Ethylene chlor-iodide also gave the oxide when heated with sodium oxide.

The properties of ethylene oxide have been further studied by several investigators. Girard[7] found that it reacted with phosphonium iodide to give, first ethylene iod-hydrin, and finally, with an excess of phosphonium iodide, ethylene iodide. Bredig[8], and later Hantsch and Hibbert[9] determined the electrical conductivity of ethylene oxide and found it to be very small.

Trimethylene Oxide.

This compound was discovered by Reboul[10], who obtained it by the action of a very concentrated solution of potassium hydroxide upon trimethylene chlor-hydrin. The volatile products obtained were condensed in a freezing mixture of ice and salt. The liquid obtained was dried over potassium carbonate and redistilled. In another experiment, he used pulverized solid potassium hydroxide instead of the solution, and he found this to be more suitable. Reboul found that the oxide prepared in these experiments was a colorless, mobile liquid, which was miscible with water and reacted very energetically with bromine. Its boiling point was given as about 50°. An analysis of the product gave the following results:

	Found	Theory
C	61.7	62.0
H	10.6	10.4

The substance contained a trace of chlorine compounds.

Polymeric Trimethylene Oxide

When water was added to the flask in which the trimethylene oxide had been generated, Reboul noticed that an oily layer separated at the surface of the potassium hydroxide solution. The alkaline residue was extracted with ether, and after removing the ether by distillation, the ether extract was distilled. A small quantity of liquid distilled from 160-170°, which he decided was the unchanged chlorhydrin. From 170-320°, nothing passed over, and the greater part of the ether extract boiled above 320°. Reboul analyzed the high boiling product and found that it contained approximately the same percentages of carbon and hydrogen as did the low boiling oxide. He decided that he had obtained a mixture of polymers of trimethylene oxide.

Tetramethylene Oxide

Dekkers,[11] and later Demjanow[12] found that the action of silver nitrate upon tetramethylene di-nitramine hydrochlorid gave tetramethylene oxide, as the principal product. They found that the purified product was soluble in water and boiled at 67°. With fuming hydrobromic acid, tetramethylene oxide gave the dibromide. The glycol was not formed appreciably by heating the oxide with water at 150°.

Pentamethylene Oxide

Demjanow[13] prepared this compound by heating the glycol with 60 percent sulphuric acid. Hochstetter[14] prepared it by heating tetramethylene bromide with water in a closed tube

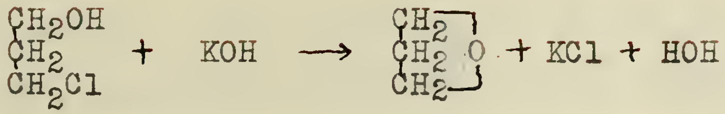
at 100°. These investigators found that pentamethylene oxide boiled at 80-82°. It was more soluble in cold water than in hot, and was, of course, soluble in alcohol and ether.

THEORETICAL

Trimethylene oxide is a four atom ring compound. According to Baeyer's strain theory, this compound should not be so stable toward rupture of the ring as the five and six atom ring oxides, tetramethylene oxide and pentamethylene oxide. This is demonstrated in this work, since it is rather difficult to prepare trimethylene oxide, while pentamethylene oxide is easily prepared by the dehydration of the glycol. Moreover, trimethylene oxide is extremely active chemically, breaking down readily to form straight chain compounds, while pentamethylene oxide is very stable to this sort of a reaction.

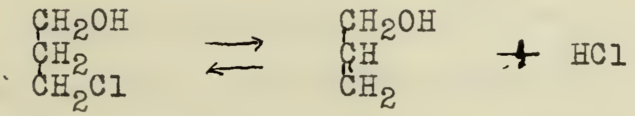
In attempting to prepare trimethylene oxide from trimethylene bromide by the action of mercuric oxide, mainly unsaturated products were produced, probably because the reaction for the formation of the oxide was a good deal slower than the reaction producing unsaturated compounds. This reaction has been studied in greater detail by Vollweiler[15].

When trimethylene chlor-hydrin is heated to 140° with potassium hydroxide, trimethylene oxide is produced according to the following reaction:



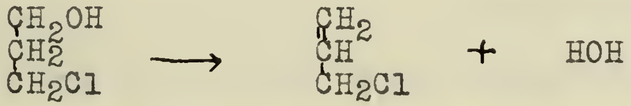
$$\begin{array}{l}CH_2OH\\ CH_2\\ CH_2Cl\end{array} + KOH \longrightarrow \begin{array}{l}CH_2\\ CH_2\\ CH_2\end{array}\!\!\Big]O + KCl + HOH$$

But if the chlor-hydrin is looked upon as an alcohol, one would expect that it would act as a dissociating medium for halogen compounds, and that trimethylene chlor-hydrin would dissociate in it according to the reaction:



$$\begin{array}{l}CH_2OH\\ CH_2\\ CH_2Cl\end{array} \rightleftarrows \begin{array}{l}CH_2OH\\ CH\\ CH_2\end{array} + HCl$$

the equilibrium being displaced by the removal of the hydrochloric acid by the potassium hydroxide. But the hot potassium hydroxide is also a dehydrating agent and removes from the molecule, thus:



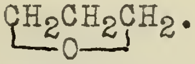
$$\begin{array}{l}CH_2OH\\ CH_2\\ CH_2Cl\end{array} \longrightarrow \begin{array}{l}CH_2\\ CH\\ CH_2Cl\end{array} + HOH$$

There are numerous other reactions that might take place under the conditions of this experiment. For instance, both the chlorhydrin and allyl alcohol would react to some extent to form their respective potassium alcoholates, each of which could in turn react with the chlor-hydrin to form ethers and unsaturated compounds, or with allyl chlorid, to form unsaturated ethers. The unsaturated compounds all undergo polymerization, and the reaction becomes extremely complicated. Reactions of the type outlined above have all been well established in analogous fields. When these are considered, it is not at all strange that it is difficult to obtain good yields of trimethylene oxide. Fortunately the only products that distill over and contaminate the

oxide are allyl chlorid, which boils at 46° and allyl alcohol, which boils at 96°. These are easily removed by bromine which reacts instantly with compounds having the ethylenic double union, forming high boiling di-bromides that are easily separated by distillation.

In using the chlor-propyl acetate instead of the chlor-hydrin, the same mechanism is followed, except that before these reactions can take place, the chlor-hydrin is liberated by the saponification of the ester with the concentrated potassium hydroxide. It is remarkable that by using the ester, the reaction for the formation of trimethylene oxide proceeds at a temperature of 110-120°, 30 degrees lower than that required for the production of the oxide by the chlor-hydrin method. This is probably due to the fact that saponification proceeds at the lower temperature, and while the molecule is in an unstable state because of the saponification, it is further attacked, and the oxide formed. Due, no doubt, to the lower temperature at which the reaction is carried out, the amount of unsaturated compounds is greatly decreased.

The oxide used in the study of the physical properties was redistilled several times after purification by the methods given below. The final product boiled absolutely constant. A qualitative test for halogens failed to reveal any trace of chlorine or bromine, while an experiment on a dilute solution of allyl chlorid, carried out in the same way, gave a decided halogen test. A vapor density on the product proved

that it was monomolecular. The method of production of the substance from the known chlor-hydrin, the action of magnesium propyl bromide forming hexanol-1, and the action of phosphorous pentachlorid giving trimethylene chlorid, all point to the atomic linking formula  $\underbrace{CH_2CH_2CH_2}_{O}$.

The results of these investigations do not agree in all particulars with those obtained by Reboul. (See page 13). For instance, Reboul found that his trimethylene oxide reacted instantly with bromine. Since in the method of purification used in this investigation bromine is used to remove the unsaturated compounds, the purified product will not be attacked by bromine appreciably in the cold during the time of purification. Moreover, it was found that after bromination had removed the unsaturated compounds, the odor of the oxide was not at all sharp as Reboul had found it , but was sweet and aromatic. Before bromination, however, the odor of the crude distillate was decidedly sharp, and repeated distillations would not remove this evidence of unsaturation. This seems to indicate that, with the small quantities with which Reboul worked, and the methods of purification used, he was not able to entirely free his product from unsaturated impurities.

The action between magnesium propyl bromide and trimethylene oxide is interesting, because it demonstrates the feasibility of using the oxide in synthetic work.

The following physical constants were determined: boiling point at 760 mm, density, index of refraction, and molecular weight.

EXPERIMENTAL

ACTION OF MERCURIC OXIDE ON TRIMETHYLENE BROMIDE.

Preparation of the Trimethylene Bromide.

To 125 gms of trimethylene glycol was added 600 gms of constant boiling hydrobromic acid. The mixture was refluxed for six hours, when an oily layer containing the trimethylene bromide was separated. The aqueous layer was again refluxed for three hours and the oil again separated. Hydrogen bromide gas was then passed into the aqueous portion for an hour, and this portion was finally distilled with steam. The distillate separated into two layers. The oil was added to the portions already separated, the whole dried over anhydrous sodium sulfate and distilled. The process yielded 270 gms of trimethylene bromide boiling at 160-170°.

Action of Mercuric Oxide on Trimethylene Bromide.

In a 500 cc round bottom flask, was placed 150 gms of mercuric oxide. At the top of the reflux condenser was a two hole rubber stopper fitted with a dropping funnel and an outlet tube. The outlet tube was connected with two U tubes, the first being empty and the second containing bromine water. The flask was heated to a temperature of 180° in the metal bath when the trimethylene bromide was dropped slowly upon the hot mercuric oxide until 125 gms had been added. It was found that about 3 cc of a volatile liquid had distilled over into the first reciever. This liquid was very mobile and had an extremely pungent odor, the fumes from the liquid attacking both the

eyes and nose. It was extremely active toward bromine. This experiment with mercuric oxide and trimethylene bromide was repeated several times, and in no case was the yield more than two or three percent of theoretical, even if the product was all trimethylene oxide, which in the light of further experimentation is extremely doubtful. Vollweiler has made a careful study of this reaction[15].

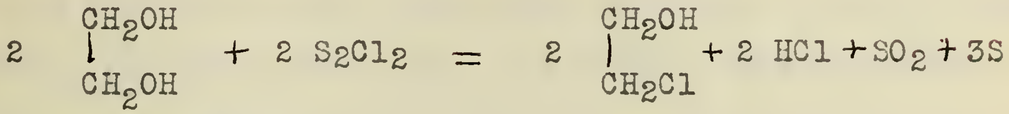
PREPARATION OF TRIMETHYLENE OXIDE BY THE CHLORHYDRIN METHOD.

Preparation of the Chlor-hydrin.[16]

Dry hydrogen chlorid was prepared by dropping concentrated sulphuric acid upon 37 percent hydrochloric acid solution, and passing the gas evolved thru concentrated sulphuric acid to remove water. The dry gas was passed into trimethylene trimethylene glycol which had been heated to 100° in a round bottom flask. At the end of three hours, the action was stopped and the contents of the flask distilled. The portion boiling between 150° and 175° contained the chlor-hydrin. This fraction was redistilled, and from 130 gms of trimethylene glycol, 25 gms of chlor-hydrin boiling at 160-164° was obtained. Practically no trimethylene chlorid was obtained, but a large amount of unchanged glycol remained in the flask. This indicates that the hydrogen chlorid was not passed into the glycol for a long enough time.

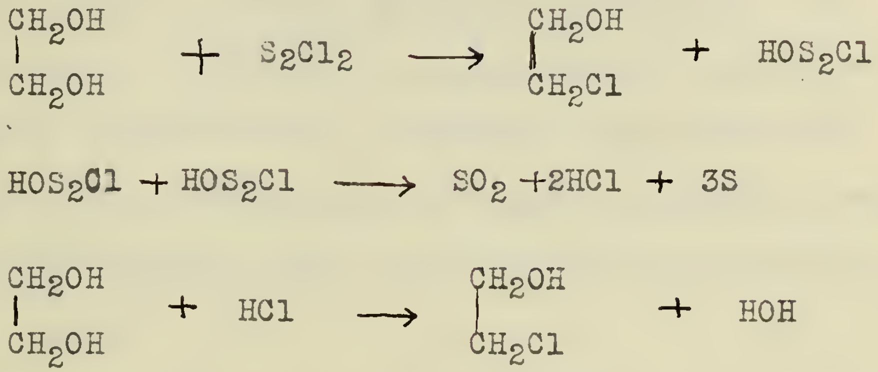
Carius[17] prepared the chlor-hydrin of ethylene glycol

by the action of sulfur chlorid on the glycol. According to his interpretation the reaction proceeds as follows.:



$$2\ \begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 2\ S_2Cl_2 = 2\ \begin{array}{l} CH_2OH \\ | \\ CH_2Cl \end{array} + 2\ HCl + SO_2 + 3S$$

Obviously, the steps are:



$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + S_2Cl_2 \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CH_2Cl \end{array} + HOS_2Cl$$

$$HOS_2Cl + HOS_2Cl \longrightarrow SO_2 + 2HCl + 3S$$

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + HCl \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CH_2Cl \end{array} + HOH$$

The proceedure in preparing trimethylene chlor-hydrin by this method is as follows:

In a liter flask was placed 230 gms of trimethylene glycol and 450 gms of sulfur chlorid. After the mixture had been shaken, it became warm and there was an evolution of sulfur dioxide, while sulfur was precipitated. Without heating, but with occasional shaking, a lively action continued for an hour. When the spontaneous action had ceased, the mixture was heated on the water bath for six hours, and finally for an hour over the free flame. By this time, sulfur dioxide had ceased to be evolved. The cessation of the evolution of sulfur dioxide is adopted as a criterion of the completion of the reaction. The contents of the flask were then cooled, and ether added. After removing the ether solution the precipitated sulfur was washed with ether.

The ether solution was then shaken with a saturated solution of potassium carbonate, to remove sulfur dioxide, the two layers separared and the ether layer dried over anhydrous sodium sulfate. After removing the ether, the crude chlorhydrin was distilled. The portion boiling 140-180° was redistilled and a yield of 160 gms of chlor-hydrin boiling 160-164° was obtained, this being about 60 percent of theory. This method is much simpler than the hydrogen chlorid method, requiring less attention. The chlor-hydrin is a colorless oil, slightly soluble in water, and having a very pleasing odor. Its boiling point is 162, under 760 mm.

Preparation of Trimethylene Oxide by the Action of Potassium Hydroxide upon Trimethylene Chlorhydrin.

The method of Reboul[10] was followed rather closely. A 500 cc flask was fitted with a dropping funnel and a thermometer so arranged that the bulb was in the reacting mixture. The side neck was connected with two U tubes in series to insure complete condensation, which were immersed in a freezing mixture of hydrochloric acid and ice. In this flask was placed 100 gms of potassium hydroxide and 10 gms of water. The temperature of the mixture was brought to 130° where it was maintained throughout the experiment. 50 gms of chlorhydrin was added drop by drop thro the dropping funnel, over a period of 45 minutes, As each drop of the chlor-hydrin struck the hot potassium hydroxide, a lively action resulted and a vapor was evolved which condensed

mainly in the first reciever.

Purification of Trimethylene Oxide

After all the chlor-hydrin had been added, the flask was allowed to cool, and water was added to dissolve the potassium hydroxide and potassium chlorid. The residue was then extracted with ether, and the ether extract worked up for high boiling products. The treatment of this residue will be discussed later.

The product which condensed in the reciever was a colorless mobile liquid, soluble in water and having a sharp odor. It was observed that the substance at this stage is very reactive toward bromine. Bromine was added drop by drop to the ice cold distillate until the permanent bromine color remained. At first the bromine acted instantly and violenely, being immediately discolored. When the permanent color had been obtained, water was added until the water layer was four times greater in volume than the oily layer. The two layers were then thoroughly shaken, to remove all soluble substances, The heavy bromide layer, which settled out on standing, was removed and the aqueous layer saturated with potassium carbonate. The solution separated into two layers, the lighter containing the trimethylene oxide. The two layers were separated, and the crude oxide dried over anhydrous sodium sulphate,and distilled from the water bath. The distillate was redistilled, and gave 2 gms of pure trimethylene oxide boiling at 48-49^{o}(uncorrected). It was noticed that the

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

sharp, unpleasant odor of the crude distillate had entirely vanished, and that the odor was now sweet and aromatic.

Several modifications of this method of preparing trimethylene oxide have been tried. An experiment was run in which the temperature withim the flask was kept at 160-180°, and the result was a preponderance of unsaturated compounds, and very little trimethylene oxide. The next modification was to use a more dilute solution of potassium hydroxide. Instead of 10 cc of water to 100 gms of potassium hydroxide, 20 cc was used. The yield of distillate was very much lessened in this case. Another experiment was run using alcohol as a solvent. Again it was found that mainly unsaturated products were formed. Moreover, a considerable quantity of ethyl alcohol distilled over with the low boiling substances, and the complete separation of the oxide was extremely difficult.

While the chlor-hydrin gave some trimethylene oxide, the quantity was so small that the method could hardly be called a feasible one. In all, seven runs were made, and the average yield was only five or six percent of theory.

PREPARATION OF TRIMETHYLENE OXIDE BY THE ACTION OF CHLORO-PROPYL ACETATE UPON POTASSIUM HYDROXIDE

Preparation of the Chloro- Propyl Acetate

A flask having a capacity of 1500 cc was connected with an upright water cooled condenser, fitted at the top

with a dropping funnel and an otulet tube leading into an absorption apparatus filled with water. In the generating flask was placed 300 gms of trimethylene chlor-hydrin. Thru the dropping funnel was added slowly 250 gms of acetyl chlorid. The hydrogen chlorid liberated was absorbed in the absorption train. After all the acetyl chlorid had been added, the contents of the flask were boiled gently, until there was no further evolution of hydrogen chlorid. The crude ester was redistilled, yielding 375 gms of chloro-propyl acetate, boiling 160-166°. This was 85 percent of theory.

Preparation of the Oxide.

The same apparatus in which the oxide was made by the chlorhydrin method was used for this experiment. 150 gms of solid potassium hydroxide was placed in the 500 cc generating flask. To this was 12 cc of water and the temperature brought to 100°, the bulb of the thermometer being immersed in the potassium hydroxide mixture. Thru the dropping funnel was then added slowly, 75 gms of chloro-propyl acetate. A lively action took place at once, and no further heating was necessary throughout the experiment. The heat of the reaction kept the the temperature of the reaction mixture at 100-110°. Continued shaking was necessary to maintain a thorough mixture of the reacting substances. In an hour, all the ester had been added, and the mixture was then heated for ten minutes at 120°. At this time a marked odor of unsaturation was noticed, and the heating was

discontinued. The experiment was duplicated and the products of the two reactions combined. The total weight of the crude distillate from 150 gms of ester was 29 gms. It was noticable that this distillate did not possess nearly so strongly the sharp odor of the allyl compounds as did the crude product obtained by the chlor-hydrin method, although this odor could still be detected. The whole was placed in a small flask kept cold by immersion in a freezing mixture. Bromine was then added slowly, a much smaller quantity being required to produce the permanent color than in any of the previous experiments. When no more bromine was acted on in the cold, the product was distilled from the water bath, and the distillate condensed in a reciever immersed in a freezing mixture. The distillate was colored slightly yellow with the excess bromine, and was allowed to stand for 24 hours in a glass stoppered bottle. At the end of that time, the color had disappeared, probably because of substitution. The crude trimethylene oxide was redistilled giving 14 gms of pure trimethylene oxide boiling 48-50° (uncor.). This is 22.5 percent of the quantity predicted by theory. Another experiment was run, using 150 gms of the acetate and 300 gms of potassium hydroxide, with 25 cc of water. The yield in this case was somewhat lessened, being 12.7 gms , or 19 percent of theory, indicating that the reaction runs better with the smaller quantities.

CHEMICAL PROPERTIES OF TRIMETHYLENE OXIDE.

It has been found by Grignard[18] that ethylene oxide acts on the magnesium alkyl halides to produce the higher alcohols. It was desirable to determine whether the higher alcohols could be synthesized by the action of trimethylene oxide upon the magnesium alkyl halides.

Magnesium propyl bromide was prepared by the action of 4.3 gms of magnesium ribbon upon 24 gms of propyl bromide in absolute ether. To this mixture was added slowly 10 gms of trimethylene oxide in 25 gms of absolute ether. The action proceeded with a hissing sound and an evolution of heat. When all had been added, the mixture was refluxed for half an hour using an upright water cooled condenser. The water was then drawn from the condenser and the ether evaporated. As the last traces of ether were evaporated, the mass became porous and metallic looking. Suddenly a violent reaction took place, throwing clouds of smoke from the top of the condenser, evolving a great deal of heat, and leaving the residue somewhat charred and in the form of a hard cake. Water was then added to the previously cooled mixture, causing a slight heating. When the product was distilled with steam, about 2 cc of an oil was obtained which had an odor much like hexanol-1. The volume of the liquid was not great enough, however to purify by redistillation.

In order to determine a means of preventing this violent decomposition of the complex, a modification of this experiment was tried. Half the above quantities were used and the

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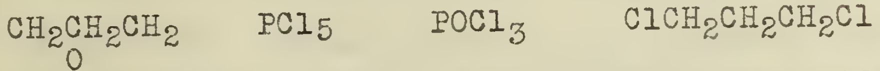
magnesium propyl bromide was prepared in the same manner as before. To the ether solution was added 5 gms of trimethylene oxide in 10 cc of absolute ether, and the mixture refluxed as before. Instead of distilling off the ether at this point, 100 cc of dry benzene was added to the mixture, and the ether distilled from this, leaving benzene as the solvent for the reacting substances. While the ether was being evaporated a thermometer was suspended in the upright condenser. When the temperature of the distilling vapors had reached 70°, the mixture was refluxed under the water cooler for four hours. The complex, which had been precipitated as a gray solid, on the addition of the trimethylene oxide, became pasty under this treatment. No change of color, however,was noticable. The mixture was now cooled and water added, without visible evidence of heat effect. As the gray mass went into solution, a white precipitate was formed at the bottom of the flask, and the liquid portion separated into two liquid layers. The precipitate was dissolved in 30 percent sulfuric acid, and the mixture distilled with steam. The distillate collected in two layers, and after separation, the oil was dried over anhydrous sodium sulfate, and redistilled. After the benzene had passed over, 5 cc of of a liquid distilling constant at 155° (uncor.) was obtained. This was identified as hexanol-1.

When trimethylene oxide was treated with phosphorous pentachlorid, a violent reaction took place, and an oil, insol-

uble in water and cold, concentrated sulfuric acid was formed. The liquid boiled at 127° (uncor.) and was identified as trimethylene chlorid, formed according to the reaction:



$$\underset{O}{CH_2CH_2CH_2} \quad PCl_5 \quad POCl_3 \quad ClCH_2CH_2CH_2Cl$$

Acetyl chlorid reacts violently with trimethylene oxide to form the chloro-propyl acetate.

PHYSICAL PROPERTIES OF TRIMETHYLENE OXIDE.

Determination of the Boiling Point.

The boiling point of trimethylene oxide was determined by the equilibrium method. The following table shows the readings taken with the thermometer, and these readings corrected for emergent stem, for calibration, and for variation of the atmospheric pressure from 760 mm.

Readings.	B.P. 760 mm.
47.35°C	47.77°C
47.45	47.87
47.40	47.82
47.50	47.92

Determination of the Density.

The density of trimethylene oxide was determined in an ordinary specific gravity bottle. Owing to the extreme volatility of the oxide, some difficulty was experienced in weighing this compound. The determinations were made at 25°.

Wt. bulb with oxide.	Wt. bulb Empty.	Vol. of bulb.	Wt. of oxide.	Density of oxide.
10.6760 gms	6.0086 gms	5.2272 cc	4.6674 gms	0.8930
10.6770 "	6.0086 "	5.2272	4.6684 "	0.8931

These densities are compared to water at 4° C.

Determination of the Index of Refraction.

The index of refraction of trimethylene oxide was determined by the Abbe' Refractometer using ordinary (white) light. The following were the readings taken:

N^{25°.	N^{25°.
1.3900	1.3892
1.3895.	1.3901
1.3899	1.3895
1.3899	1.3898
1.3897	1.3899

Determination of the Molecular Weight.

The molecular weight of trimethylene oxide was determined by the method of Victor Meyer. Three determinations were made with the following results:

Molecular Weights
61.5
56.8
55.5

The calculated molecular weight is 58.

RESIDUES FROM THE PREPARATION OF TRIMETHYLENE OXIDE.

After the trimethylene oxide had been driven from the generating flask, as has been stated once before, the residues were cooled and the water solutions extractes with ether. The ether solutions were dried over anhydrous sodium sulfate, and the ether distilled over. The remaining substances were subjected to fractional distillation. A considerable quantity of the liquid distilled over below 100°. This portion was treated with bromine and found to add that substance quantitatively. From 100- 150° little distill-

ed over, but from 150-190°, there was an increased quantity of distillate. It was this portion that Reboul considered to be the unchanged chlor-hydrin. But it was found that this fraction also reacted vigorously and completely with bromine to give a heavy oil, while the chlor-hydrin under similar conditions, will not react at all. From 200° under ordinary pressure to 270° under 30mm several fractions were obtained, all of which formed heavy additive bromides. The latter fractions were viscous oils which seemed to have minute crystals in the liquid. However, they did not crystallize further on standing for three months. The residue from this distillation was a dark yellow, viscuos mass. This also reacted with bromine, although somewhat slower. The bromination was never-the-less, complete.

CONCLUSIONS

CONCLUSIONS.

I. Normal butyl malonic ester has been characterized for the first time.

II. The action of mercuric oxide on trimethylene bromide gave mainly unsaturated compounds.

III. Chloro-propyl alcohol has been for the first time, prepared by the sulfur chlorid method.

IV. A critical study of Reboul's method of preparing trimethylene oxide from chloro-propyl alcohol has shown that his product was impure, containing allyl chlorid, and possibly other unsaturated compounds.

V. Trimethylene oxide has for the first time, been prepared from chloro-propyl acetate, and this has proven to be the best method for its preparation.

VI. The atomic linking structure of trimethylene oxide has been proven by its reaction with propyl magnesium bromide to give hexanol-1, and by its reaction with phosphorous pentachlorid to give trimethylene chlorid.

VII. The following physical constants have been determined:

Boiling point at 760 mm	47.8° (cor.)
Density at 25°. (Water at 4° 1)	0.8931
Index of refraction by Abbe'	1.3899
Molecular weight by V.Meyer	57.9

The author wishes to express his indebtedness to Dr. C. G. Derick, under whose direction these studies were carried out, for many valuable suggestions, which have, in many cases, greatly shortened the way to definite results.

BIBLIOGRAPHY

1. Hell and Lumpp, Ber 17, 2218.
2. A.Wurtz, A. Ch. (3) 55, 427 (1859).
3. A.Wurtz, A. Ch. (3) 69, 355 (1863).
4. A.Wurtz, Bull. Fr. Soc. (2) 29, 530 (1878).
5. Demole, A. 173 125, (1874).
6. Greene, C.r. 85, 624 (1877).
7. Girard, C.r. 101, 478 (1885).
8. Bredig, Ber. 35, 271 (1902).
9. Hibbert, Ber. 40, 1514 (1907).
10. Reboul, A. Ch. (5) 14, 496, (1878).
11. Dekkers, R. 9 102 (1890).
12. Demjanow, Ber. 25, Ref. 912 (1912).
13. Demjanow, J. Russ. Phys. Chem. Ges. 22, 389(1890).
14. Hochstetter, M. 23, 1073, (1902).
15. Vollweiler, Thesis, Submitted in Partial Fulfillment of of the Requirements for the Degree of Master of Arts in the Graduate School of the University of Illinois.
16. See 10
17. Carius, A. 124, 257.
18. Grignard, C. r. 136, 1260 (1903).

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